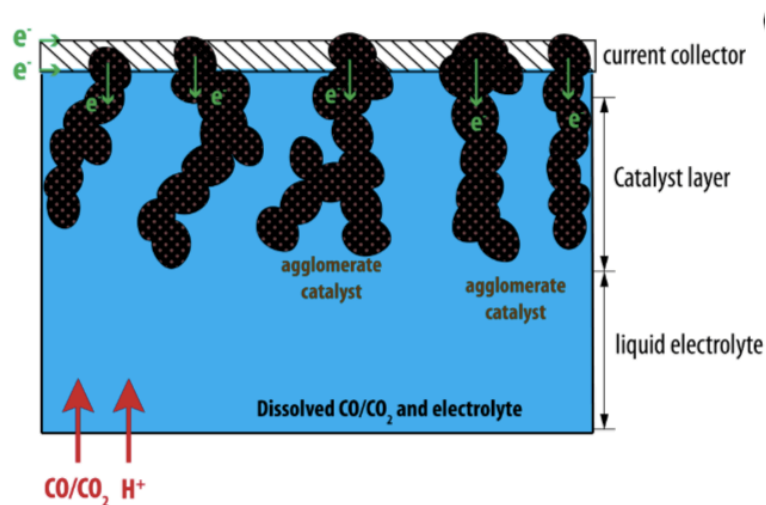


$H_2O \xrightleftharpoons[k_{1b}]{k_{1f}} H^+ + OH^-$	$k_{1f} = 10^8 \text{ s}^{-1}$ $k_{1b} = 10^{19} \text{ M}^{-1} \text{ s}^{-1}$
$H_3PO_4 \xrightleftharpoons[k_{2b}]{k_{2f}} H_2PO_4^- + H^+$	$k_{2f} = 10^7 \text{ s}^{-1}$ $k_{2b} = 1.32 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
$H_2PO_4^- \xrightleftharpoons[k_{3b}]{k_{3f}} HPO_4^{2-} + H^+$	$k_{3f} = 10^7 \text{ s}^{-1}$ $k_{3b} = 1.62 \times 10^{14} \text{ M}^{-1} \text{ s}^{-1}$
$HPO_4^{2-} \xrightleftharpoons[k_{4b}]{k_{4f}} PO_4^{3-} + H^+$	$k_{4f} = 10^7 \text{ s}^{-1}$ $k_{4b} = 4.68 \times 10^{19} \text{ M}^{-1} \text{ s}^{-1}$
$CO_2 + H_2O \xrightleftharpoons[k_{5f}]{k_{5b}} H^+ + HCO_3^-$	$k_{5f} = 0.036 \text{ s}^{-1}$ $k_{5b} = 7.83 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$
$CO_2 + OH^- \xrightleftharpoons[k_{6b}]{k_{6f}} HCO_3^-$	$k_{6f} = 2.23 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ $k_{6b} = 4.85 \times 10^{-5} \text{ s}^{-1}$
$HCO_3^- \xrightleftharpoons[k_{7b}]{k_{7f}} H^+ + CO_3^{2-}$	$k_{7f} = 2.5 \text{ s}^{-1}$ $k_{7b} = 5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
$HCO_3^- + OH^- \xrightleftharpoons[k_{8b}]{k_{8f}} H_2O + CO_3^{2-}$	$k_{8f} = 6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ $k_{8b} = 1.2 \text{ s}^{-1}$

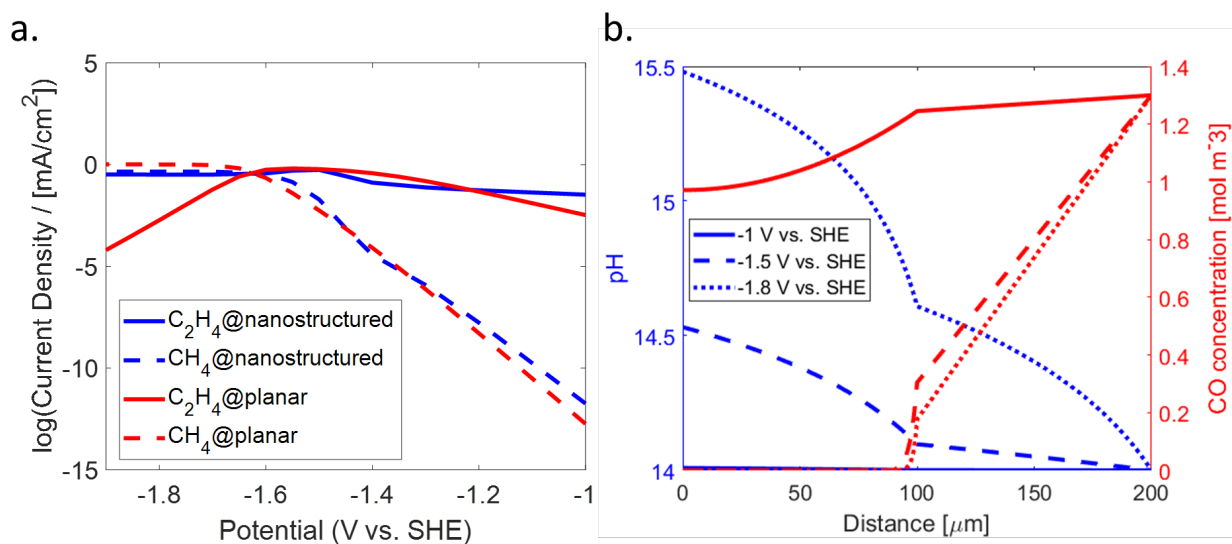
**Table S1** Forward and backward rate constants used in the modeling.

$D_{H^+}$	$9.31 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Diffusion coefficient of $H^+$
$D_{OH^+}$	$5.26 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Diffusion coefficient of $OH^+$
$D_{CO}$	$1.02 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Diffusion coefficient of CO
$D_{CO_2}$	$1.92 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Diffusion coefficient of $CO_2$
$D_{HCO_3^-}$	$1.185 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Diffusion coefficient of $HCO_3^-$
$D_{H_2PO_4^-}$	$0.879 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Diffusion coefficient of $H_2PO_4^-$
$D_{HPO_4^{2-}}$	$0.439 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Diffusion coefficient of $HPO_4^{2-}$
$D_{PO_4^{3-}}$	$0.612 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Diffusion coefficient of $PO_4^{3-}$
$D_{H_3PO_4}$	$0.879 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$	Diffusion coefficient of $H_3PO_4$
A	$1 \times 10^5 \text{ m}^{-1}$	Specific active surface area
$\alpha_e$	0.35	transfer coefficient for $C_2H_4$ formation
$\alpha_m$	1.33	transfer coefficient for $CH_4$ formation
$\alpha_{HER}$	0.258	transfer coefficient for HER
$J_e$	$1.18 \times 10^{-8} \text{ mA cm}^{-2}$	Constant present in Eq (8) for $C_2H_4$ formation
$J_m$	$3.47 \times 10^{-18} \text{ mA cm}^{-2}$	Constant present in Eq (9) for $CH_4$ formation
$i_{0\_HER}$	$0.01 \text{ mA cm}^{-2}$	Exchange current density for HER

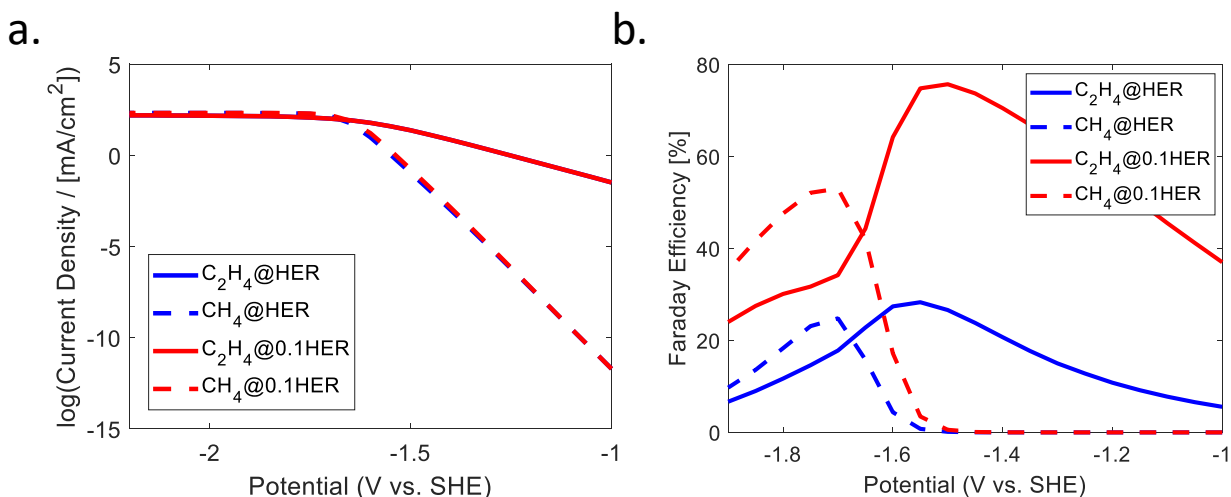
**Table S2** Kinematic parameters used in the simulations.



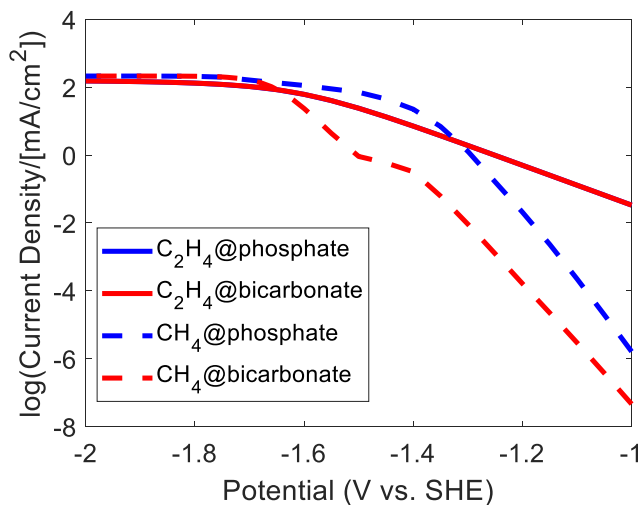
**Figure S1** A schematic illustration of a nanostructured electrode



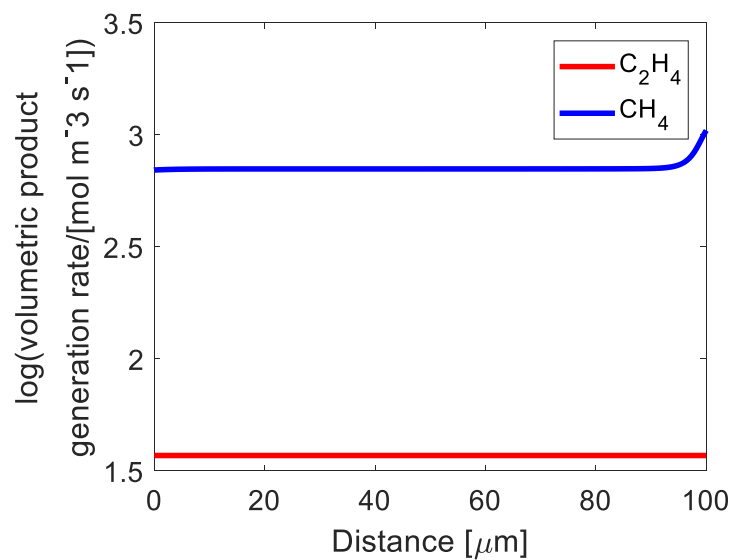
**Figure S2** (a) The geometric partial current densities for  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  generation under the initial pH of 14 in both nanostructured- and planar electrode. (b) The spatially resolved pH and CO concentration for a nanostructured at different overpotentials



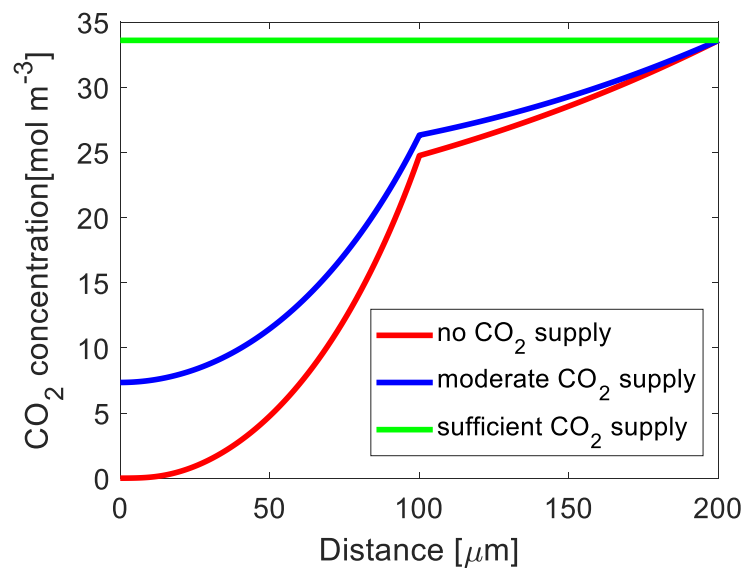
**Figure S3** (a) The geometric partial current densities and (b) The Faraday efficiencies for  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  generation under different assumptions of CO coverage in the catalyst layer (@HER stands for low CO coverage and @0.1HER stands for high CO coverage)



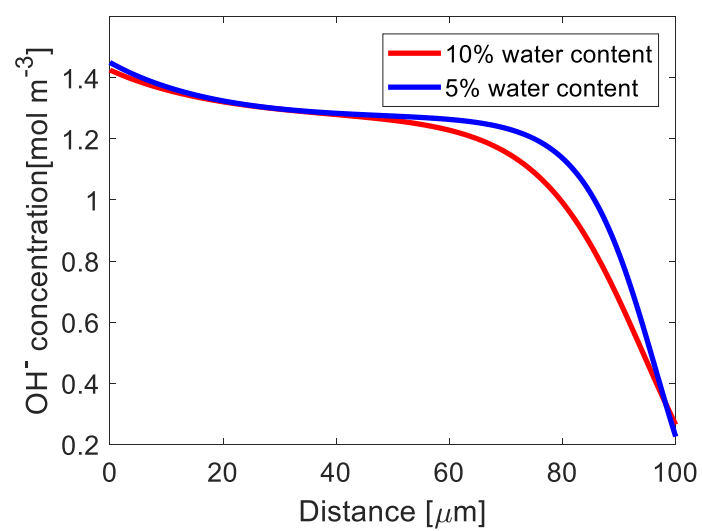
**Figure S4** The geometric partial current densities for  $\text{CH}_4$  and  $\text{C}_2\text{H}_4$  generation with phosphate buffer and bicarbonate buffer, both under the initial pH value of 8.



**Figure S5** The volumetric product generation rates from  $\text{CO}_2$  reduction as a function of position within GDE at -1.65 V vs. SHE.



**Figure S6** The  $\text{CO}_2$  concentration as a function of position inside GDEs with different kinds of  $\text{CO}_2$  supply at 1.4 V vs. SHE.



**Figure S7** The OH<sup>-</sup> concentration as a function of position inside GDEs with two different water content assumptions at -1.4 V vs. SHE.